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Studies of the Catalytic Properties of Synthetic Zeolite A. IV.[1,2]
The Thermal Stability of Silver-exchanged Zeolite A

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The effects of the degree of exchange and the dehydration upon the structural stability of silver-exchanged forms of the synthetic zeolite Linde 4A have been investigated by means of DTA, X-ray diffraction, and adsorption studies. The relative intensity of the X-ray powder diffraction decreased with an increase in the extent of Ag^+-exchange, though it indicated no accurate information on the crystallinity. An exotherm on the DTA curves which shifted to a lower temperature with the degree of exchange became an indication of the collapse of the structure; this was in good agreement with the specific surface area of the sample heated at a higher temperature. From these results, the silver-exchanged zeolite A was concluded to be thermally unstable and to lose its crystal structure at a lower temperature than the original sodium form. It is also proposed that the comparison of the X-ray powder diffraction intensity is not suitable as a method for judging the crystallinity of zeolites A.

In the previous papers of this series,[3,4] the instability of silver-exchanged zeolites A [(Ag^{ex}, Na)-A and (Ag^{ex}, Ca)-A]** was pointed out on the basis of the low intensities of the X-ray diffraction patterns and on the basis of their catalytic properties, which are quite different from those of other cation-exchanged forms. No study of the thermal stability of Ag^{ex}-A is found in the literature except that of the reduction of silver ions in zeolite. Earlier studies of zeolite A reported that the instability of zeolite A was observed in ion-exchanges involving H^+, Ba^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+} and Fe^{3+} by means of X-ray study, and that Ag^{ex}-A was stable.[5,6] However, the influence of the degrees of exchange and dehydration (heat-treatment) on the structural stability has not been systematically investigated; also, there are many ambiguous statements in the method for determining the crystallinity of cation-exchanged zeolite in the reports.

The object of this investigation was to study the thermal stability of (Ag^{ex}, Na)-A in relation to the degree of exchange. The propriety of the method for determining the crystallinity will also be discussed in relation to DTA, X-ray-diffraction, and adsorptive studies.

Experimental

Materials. The original sodium-form of zeolite A was Linde Molecular Sieves 4A (Na–A) powder. The ion exchange was carried out at 85±1 °C with a 0.1 M solution of $AgNO_3$, according to a method described before.[4] Precautions were taken to shied it from bright light during operations as much as possible, since silver-exchanged zeolite was somewhat unstable to light. The higher exchanged sample was colored only a slight gray. The (Ag^{ex}, Na)-A samples, after having been dried at 120 °C for 10 hr, were all kept over saturated NH_4Cl solutions for at least 2 weeks at room temperature to maintain the moisture content constant. The degree of exchange was determined by a method described before.[4]

X-Ray Diffraction. The X-ray powder diffraction patterns were obtained on a scintillation counter spectrometer (Rigaku-Denki Geiger flex D-9C unit) with a pen recorder, using filtered Cu $K\alpha$ radiation. The hydrated and the dehydrated samples were exposed to air while their spectra were measured. Visual comparisons of the peak intensities of certain planes were made. The (311), (321), and (322, 410) planes were chosen, as they have suitable intensities in the original Na-A.

DTA. The differential thermal analysis was performed in air using a Rigaku-Denki 8001 DTA unit, in which the temperature was raised at the rate of 10 °C/min up to 1000 °C. The α-alumina was used as the reference material.

Specific Surface Area. The specific surface areas of the samples, which were activated at various temperatures for 3 hr, were measured by a standard volumetric method, using oxygen as an adsorbate, at −196 °C. The samples were activated in two different atmospheres, *i. e.*, *in vacuo* and in air.

Results and Discussion

First, the crystallinity of Ag^{ex}-A was estimated from the X-ray diffraction patterns. The sum of the peak intensities of the (311), (321), and (322, 410) planes of Ag^{ex}-A was compared with that of the other cation forms. As is shown in Table 1, all but Ag^{ex}-A have almost the same intensity. This shows that, after ion exchange, all the hydrated samples except Ag^{ex}-A retain their primary crystal structure, as has been reported in the literature.[5,6] In many studies of zeolites, the crystallinity has thus been determined by comparing the intensities of selected X-ray powder reflections.[7]

TABLE 1. RELATIVE X-RAY CRYSTALLINITY OF HYDRATED ZEOLITES A

Cation form[a)]	% Exchanged	X-ray intensity[b)]
Na^+	100	164
K^+	79	143
Mg^{2+}	76	170
Ca^{2+}	82	148
Zn^{2+}	81	137
Ag^+	99	59

a) Cation forms other than Ag^+ were prepared in Part II.[4] b) Arbitrary units.

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** The nomenclature of the synthetic zeolites exchanged with various cations is based on the suggestions given by Barrer in the Proceedings of the 3rd International Conference on Molecular Sieves, Zurich 1973.

TABLE 2. RELATIVE INTENSITY OF (Ag^{ex}, Na)-A POWDER DIFFRACTIONS

% Exchanged $Ag^+/(Ag^+ + Na^+)$	X-ray intensity[a)] Hydrated	300 °C[b)]	600 °C[c)]
0	164	173	166
28	119		
38	105		
50	83		
57	72	61	58
84	58		
99	59	49[d)] 48	71 0[e)]
46[f)]	118		

a) Arbitrary unit. b) After heated for 3 hr *in vacuo*. c) After heated for 3 hr in air. d) 250 °C. e) 700 °C. f) $Na^{ex}_{0.54}$ $Ag^{ex}_{0.46}$-A reexchanged from uncalcined $Ag^{ex}_{0.99}$ $Na_{0.01}$-A.

The trouble is that the pattern of Ag^{ex}-A was very weak. As is shown in Table 2, the relative X-ray crystallinity of (Ag^{ex}, Na)-A decreased with an increase in the extent of Ag^+ exchanged; this trend was found also in the samples calcined at higher temperatures (up to 600 °C). This generally implies that ion exchange of Na-A with Ag^+ destroys the crystal structure, and it is contrary to Barrer's report.[6)] However, in spite of the low intensities of all the peaks every major peak of the Na-A pattern ($5 < 2\theta < 35°$) was present in the pattern of Ag^{ex}-A. We felt, therefore, that the low intensity of Ag^{ex}-A was a result of interference based on the high scattering power of silver for X-rays. This suspicion was verified by the fact that, when a sample of Ag^{ex}-A, which had never been dehydrated above 120 °C, was re-exchanged with an $NaNO_3$ solution, the Na^{reex}-A showed its peak intensity close to the original Na-A (See Table 2). It may, therefore, be concluded that the silver-exchange of Na-A does not cause the crystal to collapse and that Ag^{ex}-A may be stable thermally up to 600 °C. The most important point is that a conventional X-ray powder diffraction study (*i.e.*, a comparison of the peak intensity) of cation-exchanged zeolites A does not give accurate information on the crystallinity. A similar conclusion may also be drawn from recent reports on the stability of Ba^{ex}-A.[8,9)]

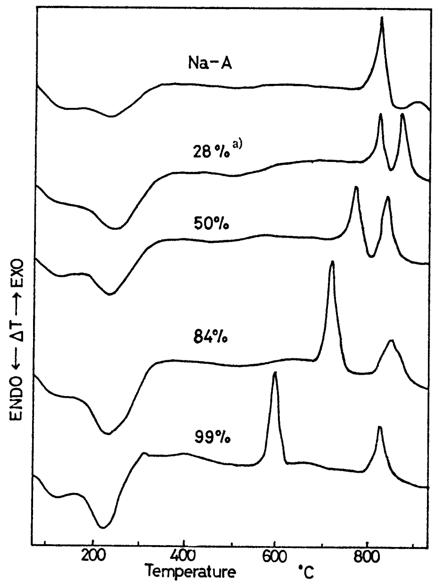

Fig. 1. DTA curves for (Ag^{ex}, Na)-A
a) The degree of exchange, $Ag^+/(Na^+ + Ag^+)$

Then, more detailed information on the stability of Ag^{ex}-A was obtained by a thermographic method. The DTA results on (Ag^{ex}, Na)-A are shown in Fig. 1. A pronounced endothermal effect (130—230 °C) and two high-temperature exothermal effects (600—910 °C) were observed in all the samples. The endothermal effect corresponds to the removal of water from the zeolite.[10)] The beginning of the first high-temperature exotherm, which is due to the loss of the structure, shifted from 780 to 560 °C with an increase in the extent of silver. In fact, the additional X-ray measurement revealed that the zeolite structure of $Ag^{ex}_{0.99}Na_{0.01}$-A is maintained until the beginning of the first exoeffect (~600 °C) and that, at 700 °C, the structure converts to the amorphous phase. This exoeffect may be considered to be due to the following reaction, caused by dehydration from structural hydroxyl groups:

$$\underset{\text{I}}{Ag(H_2O)_n\text{-Zeolite}} \overset{\Delta}{\rightleftarrows} \{\underset{\text{II}}{Ag(OH)_m\text{-Z} + AgO_x\text{-Z}} + \underset{\text{IV}}{H\text{-Z}}\}$$

$$\overset{\Delta}{\rightleftarrows} \underset{\text{III}}{AgO_x\text{-Z}} + \text{amorphous phase}$$

That is to say, the dissociation of coordinated water molecules by the polarizing power of Ag^+ and by heating releases protons, thus forming the structural hydroxyls (IV). The dehydration of IV at a higher temperature destroys the lattice structure. Since the polarizing power of Ag^+ is larger than that of Na^+, the dissociation of the protons and the hydroxyl dehydration may be promoted at lower temperatures with an increase in the extent of Ag^+ in zeolite. The process of the dehydration of IV appears on the first exotherm. This trend was in good agreement with the results obtained from the X-ray study and with the below-mentioned specific surface area.

The other exotherm appears at 850—910 °C. It is known that, at 800 °C, zeolite A recrystallizes to a β-crystobalite-type structure. The latter exoeffect, therefore, may indicate this. From these results, it may be concluded that the thermal stability of Ag^{ex}-A is lower then that of Na-A.

The specific surface area of (Ag^{ex}, Na)-A was determined from the oxygen adsorption for samples calcined at various temperatures in different atmospheres. The stability of (Ag^{ex}, Na)-A to the degree of exchange and to heat-treatment is shown in Table 3. The Ag^{ex}-A calcined at 200 °C did not adsorb oxygen. This is because of the residual water molecules coordinated strongly to Ag^+; the evidence is supported by the endotherm being sharp and larger than that of Na-A in Fig. 1. It seems that the loss of the crystallinity is slightly greater in the case of air calcination

Table 3. The specific surface area of (Ag^{ex}, Na)-A

% Exchanged	Specific surface area, m^2/g, Calcination temp. *in vacuo* 200 °C	250 °C	300 °C	400 °C	600 °C
0	385	689	659 631[a)]	616	237[a)] 36[a,b)]
28	*	664	686		
38			638		
50			653		
57			661	527	
84			451		
99	*	669	403 326[a)]	361 308[a)]	71.2[a)] <10[a,b)]

a) Recalcined at 250 °C for 30 min *in vacuo* after calcined for 3 hr in air. b) 750 °C. * Impossible to measure.

above 300 °C was smaller than that at 250 °C. This effect increases with the extent of silver exchange. We estimate that a degradation of the structure occurred to some degree, resulting in a partial obstruction of the zeolite pores to the oxygen adsorbate. Below 600 °C, however, this structural change is too samll to appear on the DTA curves. The specific surface area of Na-A calcined at 600 °C in air was still about 35% of the value at 250 °C, whereas Ag$^{ex}_{0.99}$Na$_{0.01}$-A calcined at 600 °C in air retained only about 10% of its original crystallinity. The latter change is very large, and it appears on the DTA curve (see the 99% value in Fig. 1).

The results in Table 3 (column of 300 °C) suggest that Ag$^+$ enters into sites unfavorable to maintaining the structure when the degree of exchange exceeds about 57%, since the specific surface area suddenly decreases at 84%. Zeolite A has three kinds of cation sites.[11)] Details on the site selectivity of Ag$^+$ have been reported by Nitta *et al.*[12)]

On the other hand, it is known that the Ag$^+$-exchanged zeolites are relatively reducible, easily in the dehydrated state. It was first pointed out by Habgood[13)] that the reduced Ag^{ex}-X has a partial loss of crystallinity with the appearance of metallic silver. Huang[14)] reported also that Ag^{ex}-X and Ag^{ex}-Y were reduced after treatment with CO at 350 °C. In the present case, Ag^{ex}-A exchanged highly has colored only a slight gray in the hydrated state. This may indicate a slight reduction of Ag$^+$ by light or CO in air during drying at 120 °C. However, it is considered that the reduction resulting in a collapse of the structure did not occur, because the specific surface area was retained almost the same as in Na-A and because the X-ray diffraction pattern, though low in intensity, was unchanged. Giordano[15)] also reported, from the results of DTA, that the collapse of the structure for Ag^{ex}-A calcined at 400 °C and reduced by hydrogen at 250 °C was negligible.

Furthermore, with regard to the color of Ag^{ex}-A, the sample was a white color and a slight grayish white color; it first turned a deep yellow-red color on dehydration *in vacuo* and in air at elevated temperatures. It changed to a bright yellow while cooling in air and ultimately back to the original white at room temperature. This color change occurred reversibly. Therefore, it is due to the alteration of the ligands of Ag$^+$ on dehydration, as has been described above. A study[16)] of the UV spectra of Cu^{ex}-Y at different hydration levels has revealed that, in the below reaction, the absorption band corresponding to VI appears in a longer wavelength region compared with that of V:

$$\underset{\text{V}}{\mathrm{Cu(H_2O)_6}} \overset{\Delta}{\rightleftarrows} \mathrm{CuO_3(OH)_3} \overset{\Delta}{\rightleftarrows} \underset{\text{VI}}{\mathrm{CuO_6}}$$

In the present case, three distinct complexes exist at several degrees of hydration; *i.e.*, the I, II and III described above correspond to them. According to the spectrochemical series, the absorption spectrum of Ag$^+$ in II should shift to a wavelength longer than that of I (*i.e.*, from the ultraviolet to the visible region); probably that of III would also shift to a longer wavelength region. Consequently, the Ag^{ex}-A changes from colorless to yellow-red when it is dehydrated at elevated temperatures.

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References

1) Part III: S. Matsumoto, M. Nitta, and K. Aomura, This Bulletin, **47**, 1537 (1974).

2) Presented at the Summer Meeting of the Hokkaido Branch of the Chemical Society of Japan, Kitami, July, 1974.

3) M. Nitta, K. Tanabe, and H. Hattori, *Bull. Japan Petrol. Inst.*, **15**, 113 (1972).

4) M. Nitta, S. Matsumoto, and K. Aomura, *Nippon Kagaku Kaishi*, **1973**, 1839.

5) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, *J. Amer. Chem. Soc.*, **78**, 5963 (1956).

6) R. M. Barrer and W. M. Meier, *Trans. Faraday Soc.*, **54**, 1074 (1958).

7) D. W. Breck, "Zeolite Molecular Sieves," John Wiley & Sons, New York (1974), p. 493.

8) H. S. Sherry and H. F. Walton, *J. Phys. Chem.*, **71**, 1457 (1967).

9) A. Dyer, R. B. Gettins, and A. Molyneux, *J. Inorg. Nucl. Chem.*, **30**, 2823 (1968).

10) R. M. Barrer and D. A. Langley, *J. Chem. Soc.*, **1958**, 3817

11) R. Y. Yanagida, A. A. Amaro, and K. Seff, *J. Phys. Chem.*, **77**, 805 (1973).

12) M. Nitta, S. Matsumoto, and K. Aomura, *J. Catal.*, **35**, 317 (1974).

13) H. W. Habgood, *Can. J. Chem.*, **42**, 2340 (1964).

14) Y. Y. Huang, *J. Catal.*, **32**, 482 (1974).

15) N. Giordano, S. Motelatici, and C. Zen, Recent Prog. Report, 3rd International Conf. Molecular Sieves, 1973, p. 449.

16) N. M. Kuzmenko and V. I. Lygin, *ibid.*, p. 347.